

Biodiesel from Moringa Oleifera Oil Using K-Promoted Layered Double Hydroxide Derived MgAlLa Catalysts

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Abstract

Mixed oxide catalysts derived from MgAlLa layered double hydroxide (LDH) were prepared by co-precipitation and calcination. They were characterized by the XRD, FT-IR and BET techniques. Their catalytic performance was compared with the 5%K-promoted catalyst as heterogeneous base catalysts for the transesterification of Moringa oleifera oil with methanol to produce biodiesel. At 110 °C, reaction time 6 h, methanol: oil molar ratio 30, 10 wt.% catalyst, the biodiesel with 96.1% ester content can be obtained from the 5%K/Mg_{0.70}Al_{0.11}La_{0.19}O catalyst. This solid base showed high activity without sign of catalyst leaching. M. oleifera oil appears to be an acceptable feedstock for biodiesel.

Keywords

Biodiesel; Moringa oleifera oil; Base catalyst; MgAlLaO

Introduction

The concern about dwindling worldwide petroleum reserves and the increase of environmental problems has stimulated researchers to develop alternative sources to petroleum-based fuels. Biodiesel, derived from biological resources such as vegetable oils and animal fats, is accepted in many countries as an extender or substitute for fossil based diesel, having the advantages of being biodegradable and nontoxic, with an environmentally friendly emission profile. Biodiesel possesses physiochemical properties very similar to those of petroleum-based diesel.

Thailand lacks petroleum resource for domestic consumption; hence, most of it has to be imported from overseas and crude oil prices have tendency over the years to steadily increase. Recognizing these facts, the Thai government is actively promoting the use of biodiesel as a partial, or even full, replacement for diesel. It is known that the main factor determining the cost of biodiesel is the price of refined oil feedstock,

which accounts for 88% of the total estimated production cost [1]. Some examples of biodiesel from unconventional oils include tobacco [2, 3], castor oil [4], Jatropha [5-8], and rubber seed oil [9], Camelina [10], *Terminalia catappa* L. oil [11], mahua [12], Tung oil [13, 14] and Karanja [15]. The conversion of these non-edible oils into biodiesel has been studied using mostly homogeneous alkali solutions as catalysts. Many types of heterogeneous solid base catalysts have been used [16-22].

Layered double hydroxides (LDHs) are known as anionic clays with the general chemical formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(An^-)_{x/n}.mH_2O$ where M^{II} represents any divalent metal cation, M^{III} any trivalent metal cation and An^- an anion. They have recently received much attention as solid base catalysts. The basicity could be modified either by changing the divalent to trivalent cations molar ratio $[M^{II}/M^{III}]$. LDHs have been used as heterogeneous catalysts for oil transesterification [23-24]. Calcination at appropriate temperature decomposes the LDHs into interactive, high surface area and well-dispersed mixed metal-oxides. These derived mixed metal-oxides have been used as heterogeneous catalysts for oil transesterification [25-29]. The CoMgAlLa oxides were also reported to catalyze transesterification of canola oil [30].

A way to modify the basic properties of the catalysts is by impregnation with a basic metal. In our previous work, we studied metal-loaded MgAl oxide and MgAlLa oxide for transesterification of palm oil and rice bran oil [31, 32].

In this study, Moringa oleifera oil was used as the feedstock. Moringa oleifera is the most widely known and utilized species of oilseed tree family of the

Moringaceae [33]. It is widely grown in a tropical climate and is plentiful near the sandy beds of rivers and streams. In Thailand it has been locally used for making various herbal products for medicinal purposes. *M. oleifera* seeds contain 33-41% w/w of vegetable oil [34]. It was reported as potential feedstock for biodiesel [35]. The most conspicuous property of biodiesel derived from *Moringa oleifera* oil is the high cetane number of above 60, which is among the highest reported for a biodiesel fuel [36].

In this work we synthesized mixed oxide catalysts derived from MgAlLa-LDH precursor and enhanced their basicity by promoting with K to improve the catalytic activity. Our experiments showed that these K-loaded mixed oxide catalysts are very active in the transesterification of *M. oleifera* oil with methanol. The catalysts can be readily recovered and reused. The important fuel properties of methyl esters were determined.

Materials and Methods

Materials

M. oleifera seeds were obtained from commercial supply. Pure standards of FAME were purchased from Sigma Chemical Company. All other chemicals and reagents were analytical reagent grade.

Oil Extraction

M. oleifera seeds were ground in a grinder and oil was extracted with hexane for 24 h in a Soxhlet apparatus. Hexane was removed by rotary evaporation under reduced pressure. The quality of *M. oleifera* oil was expressed in terms of the physicochemical properties such as iodine value, acid value and saponification value determined according to ASTM D5554, D5555 and D5558, respectively.

Synthesis and Characterization of Catalyst

Mg_xAl_yLa_z-LDHs ($x = 4$, $y + z = 1$ and Al/La = 4 and 1) were synthesized by an alkali-free co-precipitation method. The mixed salt solution consists of metal nitrates of Mg (NO₃)₂·6H₂O, Al (NO₃)₃·9H₂O and La(NO₃)₃·9H₂O with the designed molar ratio was added slowly to an aqueous solution of (NH₄)₂CO₃. The pH was adjusted to 11 using NH₄OH. The reaction mixture was held at 65 °C while stirring for 3 h, and then filtered and washed with distilled water. The LDHs were calcined to MgAlLaO in air at 450 °C for 15 h.

Catalyst promoted by K was prepared by impregnation. Powder of MgAlLaO was added into the solution of potassium acetate under stirring. Then, the slurry was dried and finally calcined at 600 °C for 2 h. The weight loading of K in promoted catalysts is 5 wt.% as reported in the literature for Na loaded-MgAl oxide which gave the highest activity among 0-10wt%Na studied [37].

X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku, DMAX 2002/Ultima Plus diffractometer with Cu K radiation to determine the structure and composition of the crystalline material. Surface area measurements were performed by N₂ physisorption at 77 K using a BELSORP-mini. Prior to N₂ physisorption, the samples were outgassed for 1 h at 623 K. Surface areas were calculated using the BET equation over the pressure range $P/P_0 = 0.02-0.2$, where a linear relationship was maintained. The pore size distributions were obtained according to the Barret-Joyner-Halenda (BJH) method from the adsorption branch data. Fourier-transform infrared spectra were recorded on Nicolet FT-IR Impact 410 Spectrophotometer. The samples were made into a KBr pellet. Infrared spectra were recorded between 400-4000 cm⁻¹ in transmittance mode. Mg, Al and La contents were determined using inductively coupled plasma emission (ICP) Perkin Elmer model PLASMA-1000. The soluble basicity of the catalysts in methanol was measured by the method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) [38].

Base-catalyzed Transesterification

A Parr 4590 reactor was charged with 20 g of oil, different volume of anhydrous methanol and catalyst. The mixture was stirred at 400 rpm and heated to the desired temperature. After 6 h reaction time, the mixture was centrifuged and the upper layer (methyl esters) was washed with saturated NaCl solution and distilled water to separate glycerol and soap. Anhydrous sodium sulfate was added to remove residual water in the methyl ester product. The product was analyzed by GC to determine esters content. Methyl palmitate and methyl oleate were used to determine the response coefficients of a gas chromatograph to these products. To obtain the optimum transesterification condition, the main variables, such as catalyst concentration, methanol/oil molar ratio, temperature and reaction time were investigated.

Fuel Properties of Methyl Esters

Cloud and pour point determinations were made according to ASTM D5773 and ASTM D5949, respectively. Kinematic viscosity was obtained, employing ASTM D445. Density was determined by ASTM D4052 and acid number by ASTM D974.

Results and Discussion

Synthesis and Characterization of Catalyst

In this work, the alkali-free coprecipitation method was chosen to synthesize the $\text{Mg}_x\text{Al}_y\text{La}_z\text{-LDHs}$ in order to avoid the problem of alkali contaminants in the finished catalyst that occurs in alkali coprecipitation. MgAlLa-LDHs with different content of La were synthesized, calcined and loaded with K to enhance their basic property. The successful incorporation of Mg, Al, and La within the LDHs was verified by ICP emission spectrometry. The main characteristics of the catalysts are presented in the **Table 1**. It was found that K impregnation onto the MgAlLaO decreased surface areas, pore volume and mean pore diameter of the catalysts. N_2 adsorption-desorption isotherms of MgAlLaO and K-loaded MgAlLaO (in **Figure 1**) show type IV, indicating mesoporous solid.

TABLE 1 BET SURFACE AREAS, PORE VOLUMES AND MEAN PORE DIAMETERS OF THE CATALYSTS

Catalyst	Mg/Al/La molar ratio		BET surface area (m^2/g)	Pore volume (cc/g)	Mea n pore size (nm)
	solution	solid			
MgAlLaO (A)	0.8:0.16:0.0 4	0.69:0.18:0. 13	195	0.49	10
5%K/ MgAlLaO			135	0.23	8
MgAlLaO (B)	0.80:0.10:0. 10	0.70:0.11:0. 19	158	0.33	9
5%K/ MgAlLaO			121	0.20	7

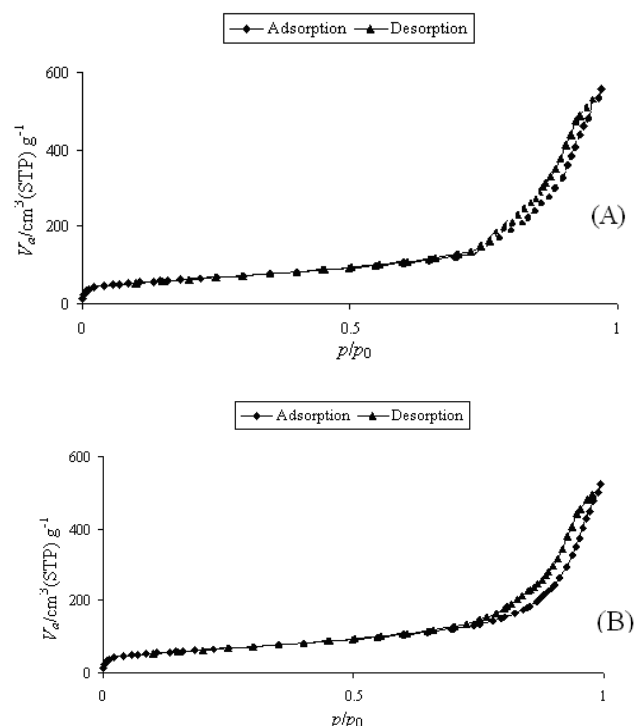


FIGURE 1 N_2 PHYSISORPTION ISOTHERMS OF (A) THE MgAlLaO AND (B) K-LOADED MgAlLaO .

The XRD patterns (in **Figure 2**) exhibit a layered double hydroxide structure with diffractions at (2), 11.6 (003), 23.2 (006), 34.8 (009), 39.2 (015), 60.8 (110) and 62.2 (113). After calcination at 450 °C for 15 h, MgAlLaO was formed. The absence of diffracted peaks of K_2O phase indicates that K species are highly dispersed in the catalyst.

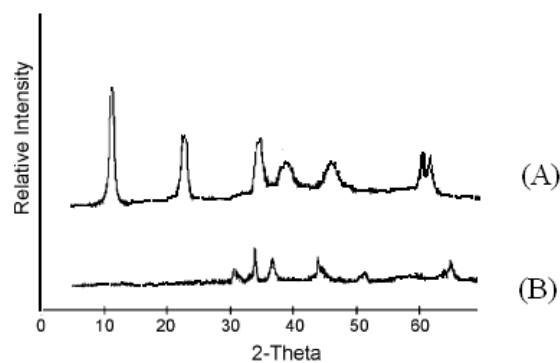


FIGURE 2 XRD PATTERNS OF (A) MgAlLa-LDH AND, (B) K-LOADED MgAlLaO

The FT-IR spectra of the MgAlLaO catalysts (not shown) show bands at 450-650 cm^{-1} from M-O stretching. A band at 1507 cm^{-1} was also observed with a low intensity, demonstrating the remaining carbonate in the catalyst, this might be due to readsorption of CO_2 from air. A broad band at 3450 cm^{-1} is ascribed to OH stretching vibration of the hydroxyl groups.

The total basicity of the catalysts was determined by

titration with acid. Results are shown in **Table 2**. As can be seen, the $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$ catalyst shows higher basicity than the $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$ catalyst. The basicity of the K-loaded catalysts increased compared to the unloaded ones.

TABLE 2 BASICITY OF CATALYSTS

Catalyst	Total basicity (mmol/g)
$\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$	0.25
5%K/ $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$	2.66
$\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$	0.38
5%K/ $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$	2.75

Extraction of *Moringa oleifera* Oil

After extraction with hexane, *Moringa* seeds were found to contain 36.5% oil. Saponification value and iodine value were 182.43 and 62.75, respectively. The oil had an acid value of 1.19 (or 0.6% FFA), fatty acids composition is shown in **Table 3**. The primary fatty acid identified was oleic acid (C18:1; 73.2%) and behenic (docosanoic, C22:0; 6.8%). Saturated acids were palmitic acid (C16:0; 5.5%) and stearic acid (C18:0; 5.7%) and arachidic (C20:0; 3.9%). Little amount of unsaturated fatty acids such as linoleic (C18:2; 1.0%) and eicosenoic (C20:1; 2.6%) acids were also present.

TABLE 3 FATTY ACID COMPOSITIONS OF MORINGA OLEIFERA OIL

	C16:0	C18:0	C18:1	C18:2	C20:0	C20:1	C22:0	others
%	5.5	5.7	73.2	1.0	3.9	2.6	6.8	1.3

Transesterification of *Moringa oleifera* Oil

The *Moringa oleifera* oil was used as the feedstock of transesterification with methanol. The influences of reaction conditions were studied to optimize the reaction condition.

Temperature is known to play an important role in biodiesel synthesis. Increasing reaction temperature not only leads to better reaction kinetics, but also improves phase miscibility, important in a potentially diffusion-limited process. The influence of reaction temperature on the transesterification reaction of *Moringa oleifera* oil with methanol was studied in the presence of K loaded-catalysts with methanol under

the condition of 6 h, methanol/oil molar ratio of 20 and 6wt.% catalyst. The effect of temperature on %ester is illustrated in **Figure 3**. Reaction temperature positively impacted the transesterification. The 5%K/ $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$ shows higher activity than the 5%K/ $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$ catalyst. The percentage of ester increased with temperature. At 110 °C, 83.5% and 76.8% ester can be obtained from the 5%K/ $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$ and 5%K/ $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$ catalysts, respectively.

Figure 4 shows methanol/oil molar ratio on the ester content with 6wt.% catalyst at 110 °C and 6 h. Excess methanol was needed even though theoretically the stoichiometry of the reaction requires 3 mol of methanol per mol of oil. This is generally ascribed to the chemical equilibrium shift. The improved oil solubility in an excess of alcohol could also favor the reaction. When the methanol/oil molar ratio was increased, the ester content was increased. At methanol/oil molar ratio of 30, 90.0% and 85.3% were obtained from the 5%K/ $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$ and 5%K/ $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$ catalysts, respectively. The excess methanol promotes the transesterification reaction and extracts products from the catalyst surface to renew catalytic sites. Thus, high ratio of methanol to oil is beneficial. However, further increase in methanol/oil molar ratio caused problem in phase separation, resulting in lower %ester content.

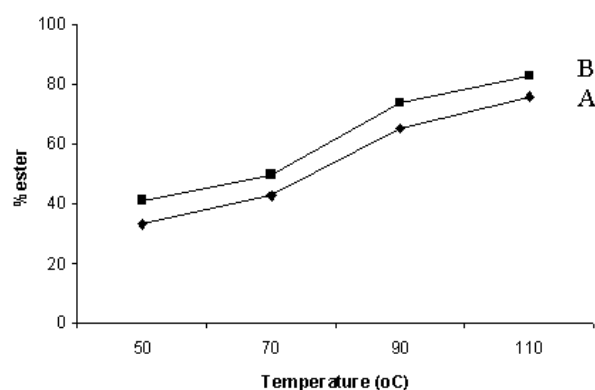


FIGURE 3 ESTER CONTENT WITH REACTION TEMPERATURE

(A) 5wt.%K/ $\text{Mg}_{0.69}\text{Al}_{0.18}\text{La}_{0.13}\text{O}$ and

(B) 5wt.%K/ $\text{Mg}_{0.70}\text{Al}_{0.11}\text{La}_{0.19}\text{O}$.

(6 wt.% catalyst, 20:1 molar ratio of methanol to oil and 8 h).

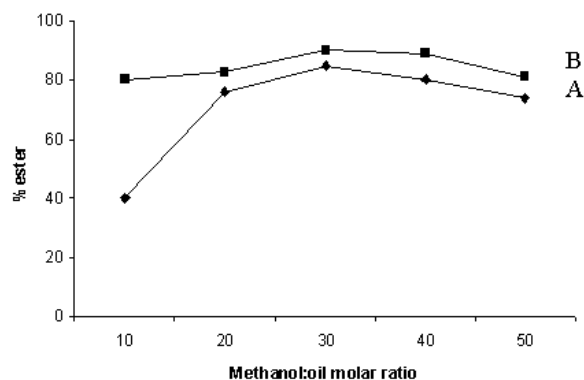


FIGURE 4 ESTER CONTENT WITH MOLAR RATIO OF METHANOL TO OIL

(A) 5wt.%K/Mg_{0.69}Al_{0.18}La_{0.13}O and

(B) 5wt.%K/Mg_{0.70}Al_{0.11}La_{0.19}O.

(6 wt.% catalyst, 8 h at 110 °C).

Figure 5 shows the effect of catalyst amount on the ester content at 110 °C and 6 h. Applying the higher catalyst amount to 8wt.% yielded the maximum ester content; 96.1% and 80.4% from the 5%K/Mg_{0.70}Al_{0.11}La_{0.19}O and 5%K/Mg_{0.69}Al_{0.18}La_{0.13}O catalysts, respectively. No significant increase of ester was obtained when the amount of catalyst was further increased.

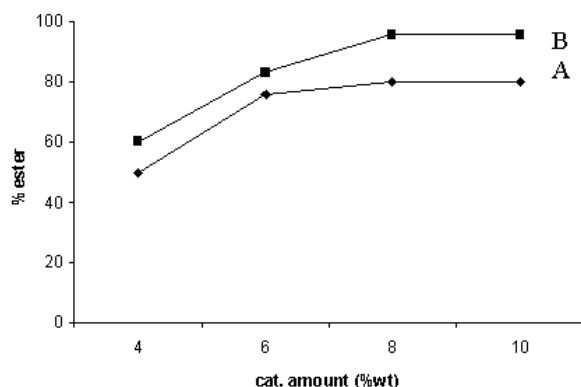


FIGURE 5 ESTER CONTENT WITH CATALYST AMOUNT

(A) 5wt.%K/Mg_{0.69}Al_{0.18}La_{0.13}O and

(B) 5wt.%K/Mg_{0.70}Al_{0.11}La_{0.19}O.

30:1 molar ratio of methanol to oil, 8 h reaction time at 110°C.

Stability and Reusability of Catalyst

For basic oxides, metal ion leaching into solution is usually a primary concern. In this work elemental analysis of the mixture after reaction showed

negligible catalyst leaching in the methanol phase. After use, the spent catalyst was separated, washed and calcined under the same conditions. It was used in subsequent reaction cycles with fresh reactants. The calcination allows an efficient recovery of the catalytic activity. The results show that the 5%K/Mg_{0.70}Al_{0.11}La_{0.19}O catalyst yielded 96.1%, 95.6 and 95.0% ester, for the first, second and third run, respectively.

Properties of Methyl Esters

Properties of *M. oleifera* methyl esters are summarized in **Table 4** together with the relevant specifications from the biodiesel standards ASTM D6751.

TABLE 4 FUEL PROPERTIES OF *M. OLEIFERA* METHYL ESTERS

Properties	Unit	<i>M. oleifera</i> methyl esters	ASTM D6751
Viscosity at 40°C	mm ² /s	4.7	1.9-6.0
Pour point	°C	5	-
Cloud point	°C	15	-
Flash point	°C	201	130 min.

Conclusions

Moringa oleifera oil is a promising source for biodiesel production and is currently not used as edible oil. The purpose of the present study was to evaluate this oil as a potential raw material for biodiesel production. *Moringa oleifera* oil was chemically converted via an alkaline transesterification process using heterogeneous basic catalysts. Potassium addition increased basicity of the catalyst, resulting in an enhancement on the catalyst activity without any sign of leaching. The use of heterogeneous catalysts reduces the costs due to simplification of process, along with minimizing the environmental problems, which is a practical alternative to soluble bases.

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